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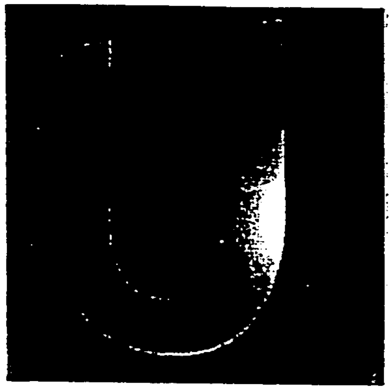

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**PIGMENTS, INORGANIC - Specialty Pigments (Heinrich Heine, Hans G. Völz, Jürgen Kischkewitz, Peter Woditsch, Axel Westerhaus, Wolf-Dieter Griebler, Marcel De Liedekerke, Gunter Buxbaum et al.)**

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⇦ Title page
⇦ Previous
⇨ References

### 4.3. Luster Pigments

As shown in Figure (47) A, *conventional pigments* interact with light by absorption and/or diffuse scattering (see Section 1.3. Color Properties). Luster pigments comprise nacreous pigments (Section 4.3.1. Nacreous and Interference Pigments) and metal effect pigments (Section 4.3.2. Metal Effect Pigments).

*Nacreous pigments* simulate the nacreous luster of natural pearls (Fig. (47) C), which consist of alternating, transparent layers of materials with a high ($CaCO_3$) and a low (protein) refractive index. Small platelets of a high-refractive-index material (i.e., the nacreous pigment) are oriented in parallel alignment in a matrix of lower refractive index, e.g., a paint binder or plastic (Fig. (47) D). Synthetic nacreous pigments are transparent or light-absorbing platelet crystals. They may also have a multilayer structure, the layers having different refractive indices and light absorption properties.

*Metal effect pigments* (Fig. (47) B) consist of small metallic flakes (mainly aluminum or Cu/Zn bronze) which act as small mirrors that reflect almost all of the incident light.

#### 4.3.1. Nacreous and Interference Pigments

Synthetic or natural pigments used to achieve lustrous, brilliant, or iridescent color effects by interference on thin optical films are called nacreous or pearlescent pigments [583][584][585][586][587]. They were originally used to simulate the appearance of natural pearls. The visual effects produced by reflection and transmittance of light by thin multilayer films are not restricted to pearls and shells but are widespread in nature [588]. Extending Greenstein's definition [584] , nacreous (pearlescent) pigments are "thin platelets of high refractive index which partially reflect and partially transmit light," or contain layers of this kind. DIN 55 943 (April 1990) proposes the comprehensive term "interference pigments" for nacreous pigments consisting of materials that do not absorb visible light (e.g., $TiO_2$) or that contain materials with a high refractive index and additional absorption characteristics (e.g., $Fe_2O_3$). However, in this article the term "nacreous pigments" is used.

The use of pearls and nacreous shells for decorative purposes goes back to ancient times (e.g., in Chinese wood intarsia). The history of pearl pigments dates back to 1656, when the French rosary maker Jaquin isolated a silky lustrous suspension from fish scales (pearl essence) and applied this to small beads to create artificial pearls [589]. It took more than 250 years to isolate the pearl essence material (guanine platelets) and understand the pearl effect [590]. Attempts were made to create synthetic pearl colors as organic or inorganic, transparent, highly refractive coatings and pearl pigments as crystalline platelets [591]. From 1920 onwards hydroxides, halides, phosphates, carbonates, and arsenates of zinc, calcium, barium, mercury, bismuth, lead, and other cations were produced for this purpose. Only the traditional natural pearl essence (Section 4.3.1.2. Natural Pearl Essence ), basic lead carbonate (Section 4.3.1.3. Basic Lead Carbonate ), and bismuth oxychloride (Section 4.3.1.4. Bismuth Oxychloride ) are still of importance.

The strong demand for pearl effects came from the growing coatings and plastics industries who wanted to improve the acceptance and popularity of their products. Furthermore, nacreous pigments also allowed artists and designers to create new visual effects similar to those found

in nature [592], [593]. The breakthrough for nacreous pigments came with the invention of mica coated with metal oxides (Section 4.3.1.5. Metal Oxide – Mica Pigments) [594]. Mica-based nacreous pigments now account for > 85 % of the world market.
Important nacreous pigments and producers are listed below:

- Natural pearl
- Engelhard Corp./Mearl, NJ, USA
- Basic lead carbonate
- J. Jaeger GmbH, Viechtach, Germany
- Polipearl S.A., Argentina
- Semo Ltd., Seoul, South Korea
- Bismuth oxychloride
- Engelhard Corp./Mearl , NJ, USA
- Rona, N.J., USA (subsidiary of Merck KGaA)
- Metal oxide – mica
- BASF, Ludwigshafen, Germany
- Kemira OY, Pori, Finland
- Engelhard Corp./Mearl , NJ, USA
- Merck KGaA, Darmstadt, Germany (and overseas subsidiaries: E.M. Industries, NY, USA; Merck Japan Ltd., Onahama, Japan)

Nacreous pigments are used to obtain pearl, iridescent (rainbow), or metallic effects, and in transparent color formulations to obtain brilliance or two-tone color and luster flops (change with viewing angle). The most important applications are plastics, coatings, printing inks, cosmetics, and automotive paints. The two major nacreous pigment producers, Merck KGaA and Engelhard Corp./Mearl, do not publish production data.
Table (41) shows an overview of pigments with luster effects. Effect pigments can be classified as metal platelets, oxide-coated metal platelets, oxide-coated mica platelets, platelet-like monocrystals, and comminuted PVD films (PVD = physical vapor deposition). Aims of new developments are new effects and colors, improvement of hiding power, more intense interference colors, increased of light and weather stability, and improved dispersibility. Of special interest are pigments which are toxicologically safe and which can be produced by ecologically acceptable processes.

### 4.3.1.1. Optical Principles

**Nacreous and Interference Pigments.** The optical principles of nacreous (interference) pigments are shown in Figure (48) for a simplified case of nearly normal incidence without multiple reflection and absorption. At the inferface $P_1$ between two materials with refractive indices $n_1$ and $n_2$ , part of the beam of light $L_1$ is reflected ($L_1'$) and part is transmitted (i.e., refracted) ($L_2$). The intensity ratios depend on $n_1$ and $n_2$ (→ Optical Materials - 2. Optical Properties of Optical Materials). In a multilayer arrangement as found in pearl or pearlescent and iridescent materials (Fig. (47) C) [585] , each interface produces partial reflection. After penetration through several layers, depending on the size and difference between $n_1$ and $n_2$ , virtually complete reflection is obtained, provided that the materials are sufficiently transparent [593].
In pigments that simulate natural pearl effects, the simplest case is a platelet-shaped particle with two phase boundaries $P_1$ and $P_2$ at the upper and lower surfaces of the particles, i.e., a single, thin, transparent layer of a material with a higher refractive index than its surroundings. For small flakes with a thickness of ca. 100 nm, the physical laws of thin, solid, optical films apply [596].
Multiple reflection of light on a thin solid film with a high refractive index (Fig. (48)) causes interference effects in the reflected light and in the complementary transmitted light. For the simple case of nearly perpendicular incidence, the intensity of the reflectance ($I$) depends on the refractive indices ($n_1$ , $n_2$), the layer thickness ($d$ ), and the wavelength ($\lambda$) [597], [598]:

$$I = \frac{A^2 + B^2 + 2AB\cos\theta}{1 + A^2B^2 + 2AB\cos\theta}$$

$$A = \frac{n_1 - n_2}{n_2 + n_1} \quad B = \frac{n_2 - n_1}{n_2 + n_1} \quad \theta = 4\pi\frac{n_2 d}{\lambda}$$

With given $n_1$ and $n_2$ the maximum and minimum intensities of the reflected light — seen as interference colors — can be calculated and agree well with experimental results[599]. Refractive indices of materials commonly used in nacreous pigments follow:

| | | | |
|---|---|---|---|
| Vacuum/air | 1.0 | $Pb(OH)_2 \cdot 2\,PbCO_3$ | 2.0 |
| Water | 1.33 | BiOCl | 2.15 |
| Proteins | 1.4 | Carbon (diamond) | 2.4 |
| Plastics | 1.4 – 1.7 | $Fe_3O_4$ | 2.4 |
| Mica | 1.5 | $TiO_2$ (anatase) | 2.5 |
| $CaCO_3$ (aragonite) | 1.68 | $TiO_2$ (rutile) | 2.7 |
| Natural pearl (guanine, hypoxanthine) | 1.85 | $Fe_2O_3$ (hematite) | 2.9 |

In practice platelet crystals are synthesized with a layer thickness $d$ calculated to produce the desired interference colors (iridescence) [599], [600]. Most nacreous pigments now consist of at least three layers of two materials with different refractive indices (Fig. (49)). Thin flakes (thickness ca. 500 nm) of a material with a low refractive index (mica) are coated with a highly refractive metal oxide (e.g., $TiO_2$ , layer thickness ca. 50 – 150 nm). This results in particles with four interfaces that constitute a more complicated, but still predictable thin film system. The behavior of more complex multilayer pigments containing additional, thin, light-absorbing films can also be calculated if appropriate optical parameters are known [599]. Color effects depend on the viewing angle [600][601][602][603][604]. Nacreous pigment platelets split white light into two complementary colors that depend on the platelet thickness. The reflected (interference) color dominates under regular (maximum) reflection, i.e., when the object is observed at the angle of regular reflection (Fig. (50) B). The transmitted part dominates at other viewing angles under diffuse viewing conditions provided there is a nonabsorbing (white) or reflecting background (Fig. (50) A). Variation of the viewing angle therefore produces a sharp gloss (reflectance) peak, and the color changes between two extreme complementary colors [600], [603]. The resulting complex interplay of luster and color is measured goniophotometrically in reflection and at different angles (→ Dyes, General Survey - 3.4. Conversion of *XYZ* Values into $L^*a^*b^*$ Coordinates) [599]. No general standard measurement geometries have yet been specified. However, colorimetric analysis always includes measurements close to regular conditions and under diffuse conditions. This can be done, for example, by tilting a standard pigmented film on a drawdown card (Fig. (50)). The colorimetric data are interpreted according to CIE $L^*a^*b^*$ data. A nacreous pigment is characterized by a minimum of three $L^*a^*b^*$ data sets measured under different conditions (e.g., 0°/45° black background, 22.5°/22.5° black background, 0°/45° white background). An

analysis of these data specifies a pigment on the basis of its hiding power, luster, and hue [602]. The influence of other measurement geometries, especially of different commercially available instruments, is discussed in [599], [600].
Against a black background or in a blend with carbon black, the transmitted light is absorbed and the reflected interference color is seen as the mass tone (i.e., overall color) of the material. In blends of nacreous pigments with absorbing colorants, the particle size of the latter must be well below the scattering limit, i.e., they must be transparent (see Section 4.4. Transparent Pigments). The nacreous effect or iridescent reflection is otherwise quenched by the hiding pigments. This also applies to blends with strongly reflecting metal effect pigments (e.g., aluminum). Blends of pigments with different interference colors obey an additive mixing law, (e.g., blue + yellow = white) instead of the subtractive color mixing of pure absorption pigments (e.g., blue + yellow = green) [600].
The behavior of combinations of interference pigments with absorption and/or metal effect pigments is too complicated to predict and requires thorough goniophotometric analysis. The nacreous pigment effects generally dominate under regular (gloss) viewing conditions, and the absorbing colorant under diffuse viewing conditions [604].

### 4.3.1.2. Natural Pearl Essence [587][589][604][605][606][607][608][609]

Natural pearl essence (Essence d'Oriente, Fish Silver) — a pigment suspension derived from fish scales, skin, or bladder — is the oldest commercial pearl luster pigment. It consists mainly of a mixture of the purines guanine [*73-40-5*] (75 – 97 %) and hypoxanthine [*68-94-0*] (25 – 3 %). The ratio of these two purines depends on the fish species (mainly herrings, sardines, and other white fish) and their geographical origin (Japan, Norway, and the northeast U.S. – Canadian coastal border).
The pigments are formed in the fish scales as platelet-shaped crystals (0.05 $\mu$m × 1 – 10 $\mu$m × 20 – 50 $\mu$m). A commercial synthetic process for producing purines with this crystal shape has not been found. An aqueous suspension of fish scales is therefore extracted with organic solvents to dissolve and remove the proteins. The remaining dispersion contains purine crystals and scale, which are separated from one other by a complicated washing and phase-transfer process [609].
Due to its tendency to agglomerate in dry form, natural pearl essence is handled as a 22 – 25 % dispersion in various media (e.g., nitrocellulose lacquer for nail enamel, aqueous or alcoholic media for lotions or shampoos) It is used almost exclusively in cosmetic applications [609].
Despite the high price, natural pearl essence has several advantages over synthetic pearlescent pigments: it is less fragile; has a low density (1.6 g/cm$^3$), which reduces settling in liquid formulations; and has a very high, but soft luster ($n$ = 1.79 – 1.91, the highest value being along the shortest axis). The world market for natural pearl essence in 1995 was estimated to be less than 50 t.

### 4.3.1.3. Basic Lead Carbonate [583][584][585][586][587], [610], [611]

The first commercially successful synthetic nacreous pigments were hexagonal platelet crystals of lead salts: thiosulfate, hydrogenphosphate, hydrogenarsenate, and most important nowadays, basic carbonate. Basic lead carbonate [*1319-46-6*] $Pb(OH_2) \cdot 2\,PbCO_3$, $M_r$ 775.7, is precipitated from aqueous lead acetate or lead propionate solutions with carbon dioxide.

$$3\,Pb(OCOCH_3)_2 + 2\,CO_2 + 4\,H_2O \longrightarrow 2\,Pb(OH)_2 \cdot 2\,PbCO_3 + 6\,CH_3COOH$$

Under appropriate reaction conditions regular hexagonal platelets (ca. 50 nm thick and 20 $\mu$m in diameter) can be obtained. The high refractive index ($n$ = 2.0), high aspect ratio (> 200), and the extremely even surface of basic lead carbonate make it an optical match to natural pearl essence.
The platelet thickness can be adjusted to produce interference colors by modifying the reaction conditions. When aligned with its plane orthogonal to the incident light, the platelet crystal behaves as a thin, solid, optical film (see Fig. (48)) with two phase-shifted reflections from the

upper and lower crystal planes (the phase boundaries).
The crystals are mechanically sensitive, and their high density (6.4 g/cm$^3$) results in fast sedimentation. In view of their agglomeration tendency and occupational health (toxicity) risks they are not produced in powder form, but are flushed from the aqueous phase into suitable organic solvents or resins and handled as stabilized dispersions.
Currently, use of basic lead carbonate is limited to artificial pearls, buttons, and bijouterie. Due to the low chemical stability of this pigment and toxicity problems, it is being increasingly replaced by bismuth oxychloride and mica-based pigments. Worldwide production of basic lead carbonate pigment in 1995 was ca. 1000 t.

### 4.3.1.4. Bismuth Oxychloride [583][584][585][586][587], [612]

Powders containing bismuth compounds have long been used for decorative purposes to generate a shiny luster or lustrous colors (e.g., facial cosmetic powders in ancient Egypt, imitation pearls made by coating glass and ceramic beads). Bismuth oxychloride [*7787-59-9*], bismuth oxide chloride, BiOCl, $M_r$ 260.4, was the first synthetic nontoxic nacreous pigment. It is produced by hydrolysis of acidic bismuth solutions in the presence of chloride ions. Precipitation conditions may be varied (concentration, temperature, pH, pressure) or surfactants added to obtain the desired crystal quality. The virtually tetragonal bipyramidal structure is thereby "squashed" into a flat platelet.
Pure BiOCl is available in three grades with different nacreous effects that depend on the aspect ratios and crystal size:

1) Low- or medium-luster powder (aspect ratio 1 : 10 to 1:15), mainly used as a highly compressible, white, lustrous filler with excellent skin feel
2) Dispersion of high luster quality (aspect ratio 1 : 20 to 1 : 40) consisting of square or octagonal platelets in nitrocellulose lacquers (nail polish) or castor oil (lipsticks)
3) Dispersion of very high luster quality (aspect ratio > 1:50) consisting of lens-shaped platelets in nitrocellulose lacquer, castor oil, or butyl acetate

Pigments consisting of BiOCl- coated mica or talc and blends of BiOCl with other organic or inorganic colorants are also available.
The dominant market for BiOCl is still the cosmetic industry. Its low light stability (it turns from silver white to metallic gray in sunlight), relatively high price, fast settling (high density, 7.73 g/cm$^3$), and mechanical sensitivity limit its use in technical applications. Although the darkening reaction is not yet understood, low-luster grades with improved light stability are available. Some manufacturers promote the combination with UV stabilizers for technical purposes. Uses are in the button industry, bijouterie, printing, and for X-ray contrast in catheters. The current world market is ca. 500 t/a.

### 4.3.1.5. Metal Oxide – Mica Pigments

The dominant class of nacreous pigments is based on platelets of natural mica coated with thin films of transparent metal oxides (see Fig. (49)). Mica minerals are sheet layer silicates and are described in detail elsewhere (→ Mica). Nacreous pigments are usually based on transparent muscovite [*99401-63-5*] but some are based on natural or synthetic phlogopite [*110710-26-4*]. Although muscovite occurs worldwide, few deposits are suitable for pigments; it is biologically inert and approved for use as a filler and colorant [613], [614].
Selection and pre-processing of the mica substrate is one of the key factors which determine the quality and appearance of nacreous pigments. The aspect ratio of the final pigment depends on the particle size distribution of the mica platelets, which have a thickness of 300 – 600 nm and various diameter ranges (e.g., 5 – 25, 10 – 50, 30 – 110 µm). Since light is regularly reflected from the planes of the metal-oxide- coated mica and scattered from the edges, brilliance and hiding power are inversely related to each other.
A mica pigment coated with a metal oxide has three layers with different refractive indices and four phase boundaries $P_1 - P_4$: ($P_1$) $TiO_2$ ($P_2$) mica ($P_3$) $TiO_2$ ($P_4$). Interference of light is

generated by reflections of all six combinations of phase boundaries, some of which are equal: $P_1P_2 = P_3P_4$, $P_1P_3 = P_2P_4$, $P_1P_4$, and $P_2P_3$. The thickness of the mica platelets varies in accordance with a statistical distribution. Consequently, interference effects involving the phase boundaries between the mica substrate and the oxide coating add together to give a white background reflectance. The interference color of a large number of particles therefore depends only on the thickness of the upper and lower metal oxide coating layers [584] , [597] , [598].

The development of the mica-based pigments started with pearlescent colors (Fig. (51) A, $TiO_2$ – mica). It was followed by brilliant, mass-tone- colored combination pigments (i.e., mica, $TiO_2$ , and another metal oxide) with one color (interference color same as mass tone) or two colors (interference and mass tone different) that depend on composition and viewing angle (Fig. (51) B). In the 1980s further development was made by coating mica particles with transparent layers of iron(III) oxide (Fig. (51) C) [615].

**Titanium Dioxide – Mica.** The first multilayer pigments were marketed in the 1960s as $TiO_2$-coated muscovite micas [586] , [594]. Two different processes are used for coating mica in aqueous suspension on a commercial basis:

1) Homogeneous hydrolysis (at 100 °C)

$$TiOSO_4 + \text{mica} + H_2O \longrightarrow TiO_2 - \text{mica} + H_2SO_4$$

2) Titration

$$TiOCl_2 + 2\ NaOH + \text{mica} \longrightarrow TiO_2 - \text{mica} + 2\ NaCl + H_2O$$

The pigments are then dried and calcined at 700 – 900 °C. The titration (chloride) process is preferred for interference pigments with thick TiO layers because it is easier to control. Chemical vapor deposition in a fluidized bed has also been proposed [616] (> 100 °C):

$$TiCl_4 + 2\ H_2O + \text{mica} \longrightarrow TiO_2 - \text{mica} + 4\ HCl$$

Only the $TiO_2$ anatase crystal modification is formed on the mica surface. Small amounts of $SnO_2$ are therefore used to catalyze conversion to the rutile structure with its higher refractive index, brilliance, color intensity, and superior weather and light resistance [585] , [586] , [587].

The sequence of interference colors obtained with increasing $TiO_2$ layer thickness agrees with theoretical calculations in the color space [599] , [617] , [618]. An experimental development of $L^*a^*b^*$ values is given in [585] (see also → Dyes, General Survey - 3.4. Conversion of *XYZ* Values into *L*a*b** Coordinates).

$TiO_2$ – mica pigments are used in all color formulations of conventional pigments where brilliance and luster are required in addition to color, i.e., in plastics, coatings, printing, and cosmetics. The major market for silver white pigments (pearl pigments, "white metallic") is the plastics industry.

Table (42) contains a comparative overview of $TiO_2$ – mica, basic lead carbonate, bismuth oxychloride, and natural fish silver pigments. Some further physical data are summarized in Table (43).

**Iron Oxide – Mica.** Like titanium dioxide, iron(III) oxide is suitable for coating mica platelets. It combines a high refractive index (metallic luster) with good hiding power and excellent weather resistance.

Commercial $Fe_2O_3$ – mica pigments are produced by precipitation of iron(II) or iron(III) ions in aqueous mica suspensions and calcination of the resulting coated particles at 700 – 900 °C [583] , [585] , [586] , [587] :

$$2\ FeCl_3 + \text{mica} + 3\ H_2O \longrightarrow Fe_2O_3 - \text{mica} + 6\ HCl$$

It is also possible to produce iron oxide – mica pigments by a direct CVD fluidized bed process in which iron pentacarbonyl is oxidized and $Fe_2O_3$ is deposited on the mica surface ( → Iron Compounds - Carbonyl Iron Oxide.) [620].

Independent of the synthesis route, iron(III) oxide crystallizes in the $\alpha$-modification (hematite)

after calcination. Brilliant, intense colors are obtained with 50 – 150 nm layers of $Fe_2O_3$ (hematite) on muscovite (see Fig. (51) C). Absorption and interference colors are produced simultaneously and vary with layer thickness. The red shades are especially intense because interference and absorption enhance each other. An intense green – red flop with different viewing angles is possible at a $Fe_2O_3$ layer thickness producing green interference (Section 4.3.1.1. Optical Principles) [621].

**Combination Mica-Based Pigments.** Simple blending of transparent absorption pigments with pearlescent pigments is only one way to attain new coloristic effects. It is possible to produce nacreous pigments coated with a layer of transparent absorption colorant to realize more pronounced brilliant colors with a sharper color flop. An additional advantage of such pigments is the elimination of dispersion problems associated with transparent absorption pigments due to their small particle size and high surface area.

One possibility for attractive combination pigments is the coating of $TiO_2$ – mica pigments with an additional layer of an inorganic or organic colorant. The thickness of the $TiO_2$ layer is decisive for the brilliance or interference effect under regular viewing conditions, whereas the transparent colorant dominates at all other viewing angles (Fig. (52)). A deep, rich color with a luster flop at all angles is attained when the colorant and interference color are matched. If the interference color and the mass tone of the colorant are different, a color flop (two-tone pigments) is seen in addition to the luster flop.

Iron(III) oxide is the most important metal oxide for combination with titanium dioxide on mica flakes. Brilliant golden pigments result which can be applied for several purposes. Two routes are used to synthesize these pigments, and different structures are formed [583] , [585] [586][587]. In the first, a thin layer of $Fe_2O_3$ is coated onto the surface of a $TiO_2$ – mica pigment. The overall interference color is the result of both metal oxide layers. The mass tone is determined by the $Fe_2O_3$ layer, and interesting gold pigments (e.g., reddish gold) are possible. In the second case, co-precipitation of iron and titanium oxide hydroxides on mica particles followed by calcination leads to greenish gold pigments. Interference and mass tone can be explained as above. The mass tone in this case is, however, further modified due to the additional formation of the highly refractive yellowish iron titanate phase $Fe_2TiO_5$ (pseudo-brookite) [622].

Other inorganic colorants used instead of iron oxide for combination pigments are $Cr_2O_3$ (green), iron blue, cobalt blue, $Fe_3O_4$ (black), and carbon black. In the case of the two black colorants, the interference color is seen as the mass tone. There is an analogy to blends with black pigments in a color formulation, where the transmitted part of the light is absorbed.

Coating of $TiO_2$ – mica with an organic colorant for a mass-tone or two-tone pigment is performed by precipitation or deposition on the mica pigment surface in aqueous suspension, assisted by complexing agents or surfactants. Another method is to fix the colorant as a mechanically stable layer by using proprietary additives.

#### 4.3.1.6. New Developments

**Coloristic Variations on the Basis of Mica.** Mica platelets can be coated with a variety of compounds to produce novel pigments. Solid-state reactions and CVD processes extend the possibilities for the synthesis of mica pigments. In addition, the calcination of the materials in the presence of inert (e.g., $N_2$, Ar) or reactive gases (e.g., $NH_3$, $H_2$, hydrocarbons) allows the formation of phases which are not producible by working in air. Table (44) contains a summary of nacreous mica pigments with special coloristic properties.

Reduction of suitable aqueous metal salts by electroless plating yields metal-coated mica pigments. They are less expensive than noble metal flakes (Au, Ag) and their brilliant metallic appearance is comparable with that of metallic flakes [585], [586].

**Functional Pigments** Initially, metal oxide – mica pigments were developed purely for their

excellent coloristic properties. Since then, they have also become of interest for functional uses. In coatings with a high content of platelet fillers, an advantageous overlapping roof-tile arrangement is possible that provides close interparticle contact, barrier effects, and dense covering. The composition and thickness of the oxide layer on the mica surface are always responsible for the physical properties like electrical conductivity, magnetism, IR reflectivity, and laser markability. Table (45)lists data on some functional metal oxide – mica pigments. **New Developments Based on Non-Micaceous Systems** The class of single crystal lustrous pigments is not limited to the nonabsorbing types like bismuth oxychloride and basic lead carbonate. Recent developments are absorbing pigments such as platelet-like graphite, laminar phthalocyanines and flaky iron oxides. These flakes consist of pure iron oxide or mixed phase pigments, e. g., $Al_xFe_{2-x}O_3$, $Mn_yFe_{2-y}O_3$, or $Al_xMn_yFe_{2-x-y}O_3$. Hexagonal platelet crystals with a diameter of 5 – 50 µm are grown under hydrothermal or flux conditions (melting) [630], [631]. They can be reduced to the corresponding isomorphous magnetites or used as substrates for additional coating with metal oxides [632].

The hematite platelets show a predominantly metallic effect. Very thin particles with a thickness of 50 – 400 nm display a pale copper gloss, which is indicative of interference. The shade can be varied and the properties of the platelets can be controlled by doping. Al or Mn is incorporated by substitution of Fe in the hematite lattice, and Si is incorporated interstitially [633]. Laminar iron oxide pigments are interesting because of their excellent fastness to light and outdoor exposure and their good mechanical stability. Their main applications up to now are in automotive paints and cosmetics.

Novel developments in nacreous and special effect pigments include the group of comminuted PVD thin films This group includes ground single-layer or multilayer film particles. The production of the film is the first step of the synthesis. In the second step, the film is ground to small platelets. Examples are pigments derived from amorphous or nanocrystalline aluminum or pigments consisting of a sequence of layers. These layers act as transmission filters towards each side; a typical sequence is as follows: a specular metal layer (e. g., Al, Cr), a dielectric layer with low refractive index (e. g. $MgF_2$), and a semi-transparent metal layer. Such compositions are known as Fabry – Perot structures [634]. The optical effect of these pigments is characterized by a very high gloss with brilliant colors. The pigments show a strong color flop when viewed from different angles. PVD film pigment can be used in the graphics industry, particularly as thin-film security device pigments in security printing [635].

Several development programs are concentrated on the search for substrate- containing systems in which mica is replaced by other platelet-like materials. For example, it is possible to replace mica by kaolin or talc and to produce bright conductive pigments by coating with $(Sn,Sb)O_2$ [636].

New pigments based on transparent silica flakes show extremely strong optical effects different to those of mica pigments [637]. Angle-dependent colors and other effects, achieved by the combination of these $SiO_2$ flakes with thin titania and/or iron oxide coating layers, have led to a new generation of pearl-luster pigments. They add a new dimension to the existing possibilities of color styling with luster pigments.

Other platelet crystals with a high aspect ratio have been reported for phtalocyanine [638], graphite [639], and 1,4-diketopyrrolopyrroles [640].

The CVD process in a fluidized bed (see Section 4.3.1.5. Metal Oxide – Mica Pigments) is also used for depositing interference $Fe_2O_3$ layers on aluminum flakes [620] as well as for the formation of titanium nitride on platelet substrates [641] or $TiO_2$ [642], [643].

Regular scattering of spherical particles (opalescence) of $TiO_2$ is also now used to generate eye-catching color effects [644], [645].

### 4.3.1.7. Uses

Nacreous and interference pigments are used as colorants or part of color formulations for all

applications where traditional pigments are used, but where additional color depth, brilliance, iridescence, color shift (flop), and other spectacular effects are desired [646]. Mica-based pigments dominate; their combination of pearl and interference effects, brilliance, stability, and weather resistance is unsurpassed. Furthermore, they are nontoxic [614].

Nacreous pigments require transparent or at least translucent binders or other carriers. Formulations with other pigments have to take their transparency and color mixing rules into account. Producers specify certain product lines for specific applications on the basis of national regulations and technical considerations. They also provide handling guidelines and base formulas.

Color systems with nacreous pigments can be formulated in four ways [604]:

1) Blending nacreous pigments with other pigments in a single-color formulation
2) Using a two-layer coating system in which the upper coat contains the nacreous pigment and the lower coat contains the hiding absorption or metal effect pigments
3) Using a two-layer system with a transparent absorption color formulation applied on top of a layer containing the nacreous pigment
4) Using a multilayer nacreous pigment consisting of an absorbing and/or iridescent coating applied in a single coat to the substrate in the form of platelets (see Section 4.3.1.5. Metal Oxide – Mica Pigments)

Special care must be taken to ensure parallel alignment of the platelet pigments during application. In plastics formed by injection molding, parallel alignment is hindered by the high viscosity of the polymer melts. Flow lines can be avoided by appropriate die/mold design and surface patterning. In coatings [647] , [648] and printing inks [649] , proper formulation, rheology control, settling and shrinking of the films on drying result in parallel, stacked alignment of the platelets. In automotive coatings [650] additional surface modification of the pigments is used to increase long-term weather resistance [651][652][653].

For ceramic applications the pigment is coated with an additional $SnO_2$ layer to stabilize it against the aggressiveness of the frits at high temperature [654].

Cosmetic applications require specific nacreous and interference pigments that are approved for use by national regulations [655] , [656]. Nacreous pigments are not used in cosmetics solely for their optical effects. $TiO_2$ – mica can be used as a sunscreen because $TiO_2$ strongly absorbs light in the near UV region [657]. A large variety of surface modifications and additives (e.g., monodisperse, submicron spheres of $SiO_2$) are used to improve processability, control oil absorption [658] , and give a softer skin feel [659].

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